(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 057 098 A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 82300358.7

(22) Date of filing: 25.01.82

(51) Int. Cl.³: H 01 B 3/28
H 01 B 3/46, H 01 R 13/447
C 08 L 83/04, H 01 J 29/90
H 01 T 13/38

(30) Priority: 26.01.81 US 228280

(43) Date of publication of application: 04.08.82 Bulletin 82/31

(84) Designated Contracting States: AT BE CH DE FR GB IT LI LU NL SE

(71) Applicant: BLASIUS INDUSTRIES, INC.
160 Norhtfield Road
Bedford Ohio 44146(US)

(72) Inventor: Hall, Harold Eugene
14767 Madison Road
Middlefield Ohio 44062(US)

(74) Representative: Wain, Christopher Paul et al,
A.A. THORNTON & CO. Northumberland House 303-306
High Holborn
London WC1V 7LE(GB)

(54) Anti-tracking material for high voltage applications.

(57) Anti-tracking materials for high voltage applications, such as for anode cups for cathode ray tubes and insulator caps for spark plugs, are made by curing compositions of the invention comprising an elastomer, preferably a curable silicone rubber, a curing agent, and an oil, preferably a silicone oil, which is incompatible with the elastomer. The oil thus remains as such finely dispersed throughout the insulator. The compositions of the invention may also include mineral fillers such as hydrated alumina and silica, and optionally other materials.

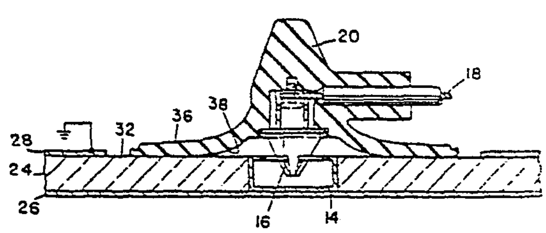

Fig. 2

EP 0 057 098 A1

Croydon Printing Company Ltd.

ANTI-TRACKING MATERIAL FOR HIGH VOLTAGE APPLICATIONS

This invention pertains to the art of electrical insulating compositions and, more particularly, to anti-tracking materials for high voltage applications.

The invention is particularly applicable for use in the anode cups used to feed high voltages to the anode through the side of a cathode ray tube of the type used to provide colour television pictures, and will be described with particular reference thereto although it will be appreciated that the invention has other and broader applications, for example, in insulating caps used on spark plugs of ignition type internal combustion enginges or in any other application where high voltage electrical insulation must exist along two abutting surfaces of electrically insulating materials.

Anode cups normally consist of a metal clip connected by an insulated wire to a source of ultra-high voltage, e.g. 20 kilovolts or more, and positioned inside a circular disc of a flexible rubber-like insulating compound having a smooth shallow concave lower surface. The clip engages a button in the side of a cathode ray tube functioning as the picture tube in a television receiver or the like, and the smooth lower surface of the disc is pressed into firm pressure engagement with the outer surface of the glass of the tube. Immediately surrounding the outer edges of the disc is a metal coating on the surface of the tube, which coating is connected to negative ground (earth). Thus, in the short distance between the button (or clip) and the grounded metal coating, there is a very high voltage gradient. As the voltage applied to the anode button increases, a voltage is reached where the path between the anode button and metal shield along the surface of the anode cup ionizes and an electric arc or spark results. This is known as the breakdown voltage. The maximum breakdown voltage which has heretofore been able to be reliably achieved is 40 kilovolts.

The undersurface of the anode cup or disc is made as smooth as possible and is held in firm pressure engagement with the outer surface of the tube to eliminate any air pockets in the interface which can ionize and lower the breakdown voltage. It has been easy to make the lower surface of the cup ultra-smooth by so configuring the surface of the moulding disc. However, as a result of the manufacturing process, the cathode ray tube glass surface has always had slight surface irregularities which result in tiny air pockets in the interface. The presence of such air pockets has limited the maximum breakdown voltage as the air can ionize to form a track.

When the breakdown voltage is exceeded, the heat generated by the arc (or spark) burns or chars the surface of the anode cup and/or etches a line in the glass surface if the picture tube. This is known as tracking. Once tracking has occurred, the breakdown voltage is substantially lowered and replacement of the anode cup is usually required.

For brighter pictures on a television picture tube, efforts have been made to increase the anode voltage beyond the 40 kilovolts heretofore employed. To date, the breakdown voltage of the anode cup has been the limiting factor in the maximum anode voltage which can be supplied to the picture tube.

A further place where breakdown voltages have become important is in the ignition systems of internal combustion engines. Here it is conventional to provide a metal clip connected to a source of high voltage and positioned in a rubber-like cup which fits like a cap over the insulator of the spark plug to prevent the high voltages from ionizing a path from the high voltage terminal of the spark plug to the grounded metal base of the spark plug and causing an arc (or spark). In recent years, efforts have been made to increase the voltage applied to spark plugs in an effort to increase the efficiency of combustion and to reduce pollutants. The ability of the cap to prevent the ionization of the path from the plug terminal to ground, and thus the formation of an external spark or track, has been a limiting factor on the maximum voltage which can be supplied to the terminal.

Heretofore, various formulations have been developed for anode cups and spark plug boots to increase tracking resistance. A typical elastomer used is produced as a proprietary product by The General Electric Company and identified by their product code SE5559U. It is a methyl silicone rubber designated ASTM VMQ. This is a flame retardant, high dielectric material. Alumina trihydrate is often added as a filler in the fabrication of anode cups because such material appears to increase the arc resistance of the finished part.

We have now found that anti-tracking materials for high voltage applications can be made with improved properties by curing certain curable elastomer compositions. The materials so made can provide very high breakdown voltages (in excess of 40 kv) and also have a self-healing property in the event that the breakdown voltage is exceeded.

According to the invention, there is provided a composition for making electrical insulators, which comprises a curable elastomer, a curing agent, and an oil incompatible with said elastomer dispersed throughout said elastomer.

The invention further provides an electrical insulator made by curing such a composition.

The invention also includes a process for fabricating a high voltage insulator, which comprises:

forming a mixture of a silicone rubber, a mineral filler, a curing agent for said silicone rubber and a silicone oil incompatible with said silicone rubber;

charging said mixture into a mould; and

applying heat to said mould thereby to cure said mixture into a solid elastomer having said liquid silicone oil dispersed throughout.

The compositions of the invention are well suited to be formed into flexible caps or cups, for example, or other form of insulator. The preferred elastomers are silicone rubbers which are preferably used with silicone oils. Among the preferred such elastomers are methyl-silicone rubbers and methyl-vinyl silicone rubbers, and phenyl-silicone oils and phenyl-methyl-silicone oils.

Among the preferred compositions of the invention are:

	Ingredients	Weight Percent
1.	Silicone Rubber	40-99%
	Mineral Filler	0-60%
	Curing Agent	0.5-03%
	Silicone Oil (incompatible with said silicone rubber)	0.25-20%
2.	Vinyl-methyl silicone rubber	60-90%
	Mineral Filler	0-40%
	Curing Agent	0.5-03%
	Silicone Oil (incompatible with vinyl-methyl silicone rubber)	0.25-05%

A particularly preferred composition comprises a methyl silicone rubber, ASTM, class MQ, or vinyl methyl silicone rubber, class VMQ; a reinforcing filler; a curing agent; and a non-compatible silicone oil.

The insulators formed from compositions of the invention are particularly adapted for use in abutting engagement with other insulators.

Tests have shown that the non-compatible silicone oil remains in the liquid form when the compositions of the invention are cured, and continuously bleeds out of the insulator body, e.g. the cup or cap, on to its surface(s). In effect, the surface(s) continuously have an oily feeling and if they are dried or wiped off, they soon regain the oily feeling. The surface silicone oil appears to fill any voids in an abutting interface of the insulator and an opposite insulating surface, thus eliminating any air pockets which heretofore have limited the maximum breakdown voltage. Further, it has been found that if there is a breakdown which causes tracking and which would normally result in a permanent lower breakdown voltage, the non-compatible silicone oil bleeds out of the insulator, fills the track and, in a few hours, the breakdown voltage has been risen again, and in 24 hours has been restored substantially to its original value. In the case of anode cups for television picture tubes, breakdown voltages can be achieved in excess of 60 kilovolts.

As stated earlier, the compositions of the invention may be used to make anode cups, spark plug boots, and to make insulation and shielding for other high voltage applications.

In order that the invention may be more fully understood, preferred embodiments thereof will now be described with reference to the accompanying drawings, wherein:

FIGURE 1 is a perspective view of an anode cup ...

in place, used to shield and insulate the anode connection on a television picture tube or cathode ray tube; and

FIGURE 2 is a cross-sectional view taken along the line 2-2 of Figure 1 illustrating an anode cup in section.

Referring now to the drawing, Figures 1 and 2 show a cathode ray tube 12 having a standard anode button 14 embedded in its side and an anode connector comprised of an anode clip 16, an anode wire 18 and an anode cup 20.

Cathode ray tube 12 is conventional and is comprised of a thick glass tube envelope 24, a metal inner layer 26, a metal grounded outer layer 28 and an open glass surface area 32 in the area of and surrounding the anode button 14. The surface area 32 is not a polished surface and is somewhat textured.

The anode to cathode voltage in a colour television set is typically in the range of 25 to 50 kilovolts DC. Insulation of the anode connection is therefore required to prevent corona discharge, arc over to the layer 28, and danger to consumers from contact with a high voltage source. Because of the high voltages involved, ionization of any air pockets between the anode button and the outer layer can result in such an arc being formed with resultant damage to the cup and/or tube.

Silicone rubber anode cups are shaped to provide a shield surrounding the anode connection. The anode cup 20 has a skirt 36 with an extremely smooth undersurface 38. Skirt undersurface 38 is pressed against the contour of the glass surface 32 thereby minimizing trapped gas between the skirt and the glass plate which could ionize. Because surface 32 is not perfectly smooth, not all air can be excluded. The interface between the glass surface 32 and the anode cup 20 is the shortest path from anode button 14 to grounded outer layer 28, and it is critical that insulation be maintained at this interface.

Shielding has not always been successful in the past. Ionization of gas or air trapped between the skirt 36 and the glass surface 32 results in paths of lower tracking or arc resistance. Tracking can occur along these paths. Once tracking occurs, the skirt undersurface 38 is charred, providing a permanent path of less resistance for further arcing between the anode connection and the grounded surface 28.

In the present invention cap 20 is fabricated from a novel composition which overcomes many of these objections.

The composition is preferably comprised of: a silicone rubber compound formulated to have the desired flexibility and chemical properties needed for the cap; a filler such as alumina trihydrate ($Al_2O_3 \cdot 3H_2O$) which increases the tracking resistance of the silicone rubber compound selected; a curing agent reactive with the silicone rubber compound selected; and a silicone oil that is incompatible with the silicone rubber used. The formulation is shaped and heat cured by transfer moulding or a similar process. The resulting part is comprised of all the ingredients (except the silicone oil) combined into a solid phase, and the incompatible silicone oil in the liquid phase dispersed throughout the part. The incompatible oil does not react with silicone rubber or filler or go into solution. Instead, it remains liquid and can migrate through the solid phase to the surface of the cured rubber part after fabrication. The surface of the moulded part has an oily feel to the hands which can be wiped dry but which will in time regain its oily feel.

This incorporation of an incompatible silicone oil in the silicone rubber part has far-reaching and unexpected results.

First, the voltage at which tracking failure occurs is greatly increased. In an anode cup fabricated from a formulation not including silicone oil, breakdown occurred at 40,000 volts through tracking to the perimeter under controlled test conditions. The physically identical part including an incompatible silicone oil tested under identical circumstances did not break down at test voltages exceeding 60,000 volts.

Second, the silicone oil gives the cup 20 the ability to recover from tracking breakdown. A typical tracking breakdown occurs between the glass surface 32 and the underside of the skirt 38. A conductive track is formed at this interface and this conductive track heats and breaks down the undersurface of the skirt 38 and etches glass surface 32. This charred track subsequently provides an area of lowered resistance to tracking breakdown permanently impairing the anode cup 20. In the present invention, with the silicone oil added, the incompatible silicone oil migrates to the affected area, filling the area with the oil, thereby excluding ionizable gases, and returning the cup to its original tracking resistance strength. We have found that the present invention allows a silicone anode cup to return to 80% of its tracking resistance strength within the first ten minutes. Twenty-four hours after failure, the cup is returned to full tracking resistance strength.

Specific formulations found satisfactory in practice are given below.

FORMULATION 1

AN ANODE CUP FORMULATION

The following ingredients are formulated in the following percentages by weight:

Ingredients	Percent
1. Silicone Rubber Compound SE 5559 U (a General Electric proprietary formulation)	55.0
2. Silicone Rubber Gum SE 435 (a General Electric proprietory formulation)	10.5
3. Reclaim	13.7
4. Alumina Trihydrate	10.5
5. Silica Filler	7.0
6. 2,5-Dimethyl-2,5-Di(t-butyl-peroxy) hexane	1.0
7. MR-1 (a proprietary formulation of Dow-Corning Corporation)	1.0
8. Silicone Oil - Dow-Corning 550 Fluid	1.3
Total	100.0

Both silicone rubber compound SE 5559 U and silicone rubber gum SE 435 are unvulcanized methyl-vinyl-silicone rubbers. SE 5559 U is a "straight" elastomer without reinforcing fillers, extending fillers or processing aids added. SE 435 is an "R-Gum" already containing fillers and processing aids. Other methyl-vinyl-silicone rubbers could be used in the place of these two materials. The two specified materials are selected to provide the flexibility and other physical properties desired in the finished product. General Electric SE 5559 U also provides the added property of flame retardance. General Electric SE 435 readily accepts fillers such as alumina trihydrate used herein.

Both of the above-described elastomers are identified as Class VMQ by the American Society for Testing and Materials (ASTM). The nomenclature used here is set forth in ASTM Standard B-1418-79a wherein the classification is identified as "silicone rubber having both methyl and vinyl constituent groups on the polymer chain". Numerous elastomers in this class are available from sources such as Dow-Corning Corporation of Midland, Michigan, The Stauffer Chemical Corporation and others.

Elastomers such as Class MQ, methyl-silicone rubbers, can also be fabricated with incompatible silicone oils to improve anti-tracking characteristics in accordance with the present invention. However, the VMQ class of silicone rubbers is best suited to the applications to which the present invention is primarily addressed.

The third listed ingredient, Reclaim, is recycled scrap of the same formulation. Scrap parts, mould flash, and other trimmings, are recycled by adding them to the formulation after devulcanizing.

The fourth ingredient, alumina trihydrate, is a mineral filler available from a great number of sources known to improve the tracking resistance of silicone rubber compositions.

Silica filler is a high purity, finely divided, silicon dioxide or sand used in silicone rubber compositions. An acceptable grade is available from the Pennsylvania Glass Sand Corporation under the trade mark Min-U-Sil.

2,5-dimethyl-2,5-di(t-butyl-peroxy) hexane is a peroxide cross linking agent used to cure or vulcanize the silicone rubber compound. Numerous other curing agents are available. However, the preferred embodiment uses the above formulation obtained from the R. T. Vanderbilt Company, Inc. under the trade mark Varox.

MR-1 is a modifier used to improve the mould release characteristics of complex parts fabricated from the above formulation. The incompatible silicone oil also adds to the mould release characteristics of the formulation and the MR-1 is not necessary in the formulation unless exceedingly complex shapes are to be fabricated.

The silicone oil specified in the formulation is a phenyl-methyl-silicone oil. It is incompatible with the silicone rubber formulation used and (after the silicone rubber cures) will remain in the liquid phase dispersed throughout the solid phase part. The silicone oil can migrate through the solid phase of the part after curing. This incompatibility and migration forms the heart of the present invention allowing a part to exude a dielectric liquid filler into any air space in the elastomer-glass interfaces and also into damaged areas in such interfaces to repair tracks formed by arcing failure.

The phenyl-methyl-silicone oil used in this embodiment has excellent electrical characteristics as well as incompatibility with the silicone rubber compound used. Thus, the high dielectric properties of silicone rubber are maintained at elastomer-glass interfaces and also in repaired track areas.

Most phenyl silicone oils and many other silicone oils are incompatible with Class VMQ or Class MQ elastomers. Any of these oils having suitable electrical and physical characteristics can also be used in the invention. The solubility of the selected oil in the selected rubber compound must be very low. Further, the silicone oil must be selected so as not to form a gel or other structure with the filler used nor to cure when subjected to the moulding or curing temperatures of the elastomer.

The proportions of the above formulation can be modified to produce a finished composition of differing characteristics.

A second formulation particularly suited for fabrication of spark plug boots is set forth below:

FORMULATION 2

A SPARK PLUG BOOT FORMULATION

Ingredients	Percent
1. 30 durometer reinforced silicone rubber gum	54.8
2. Reclaim	11.0
3. Aerosil 200 vs	2.9
4. Min-U-Sil (5 micron)	27.3
5. Red iron oxide	1.1
6. 2,5-Dimethyl-2,5-Di(t-butyl-peroxy) hexane	0.7
7. Silicone oil	2.2
Total	100.0

The first ingredient, a 30 durometer reinforced silicone rubber gum is similar to Ingredient Number 2 in Formulation Number 1. Both of these gums are reinforced rubber gum compositions available from numerous sources such as General Electric and Dow-Corning Corporation. The two ingredients differ in that Ingredient Number 2 in Formulation Number 1 is a 35 durometer while Ingredient Number 1 in Formulation Number 2 is a 30 durometer, a softer more flexible material.

Ingredient Number 2 is recycled scrap of the same formulation.

Ingredients Number 3 and 4 are silica fillers which reinforce the elastomer and improve its electrical characteristics.

Ingredient Number 5, red iron oxide, improves the high temperature characteristics of the elastomer. This is called for because of the high temperature environment of spark plug boots at internal combustion engine cylinder heads.

The curing compound Varox is the same for both formulations.

The silicone oil can be the same oil as Formulation 1 or a similar oil. In Formulation Number 2 the silicone oil is present in slightly higher amounts. Here again, the silicone oil will be exuded from the part repairing any tracking failure damage and filling the area between the boot itself and the spark plug insulator excluding air. The porcelain insulator portion of a spark plug presents a surface to the spark plug boot which is similar to the surface of a cathode ray tube presented to an anode cup.

The silicone oil in Formulation Number 2 operates in the same manner as in Formulation Number 1 to form a high voltage shield at the interface by exuding from the boot to fill any voids and repair any tracking damage.

CLAIMS:

1. A composition for making electrical insulators by transfer moulding or similar fabrication techniques, which composition comprises a curable elastomer, a curing agent, and an oil incompatible with said elastomer dispersed throughout said elastomer.

2. A composition according to claim 1, wherein said elastomer is a silicone rubber and said oil is a silicone oil.

3. A composition according to claim 2, wherein said silicone rubber is a methyl-silicone rubber or a methyl-vinyl silicone rubber.

4. A composition according to claim 2 or 3, wherein said silicone oil is a phenyl-silicone oil or a phenyl-methyl-silicone oil.

5. A composition for making electrical insulators by transfer moulding or similar fabrication techniques, which composition comprises the following ingredients by weight percentage:

Ingredients	Weight Percent
Silicone Rubber	40-99%
Mineral Filler	0-60%
Curing Agent	0.5-03%
Silicone Oil (incompatible with said silicone rubber)	0.25-20%

6. A composition according to claim 5, wherein said silicone rubber is a methyl-silicone rubber or a vinyl-methyl-silicone rubber.

7. A composition according to claim 6, wherein said silicone oil is a phenyl-silicone oil or a phenyl-methyl-silicone oil.

8. A composition according to claim 5,6 or 7, wherein said silicone oil is present in the range of 0.5 to 5%.

9. A composition for making electrical insulators, by transfer moulding or similar fabrication techniques, which composition comprises the following ingredients by weight percentage:

Ingredients	Weight Percent
Vinyl-methyl silicone rubber	60-90%
Mineral Filler	0-40%
Curing Agent	0.5-03%
Silicone Oil (incompatible with vinyl-methyl silicone rubber)	0.25-05%

10. A composition according to claim 9, wherein said silicone oil is a phenyl-silicone oil or a phenyl-methyl-silicone oil.

11. A composition according to claim 9 or 10, wherein said silicone oil is present in the range of 0.75 to 4.0%.

12. A composition according to claim 11, wherein said silicone oil is present in the range of 1.0 to 3.5%.

13. An electrical insulator made from a composition as claimed in any of claims 1 to 12, which composition has been cured.

14. A high voltage insulator, for example an anode cup for a cathode ray tube or an insulating cap for a spark plug, made from a composition as claimed in any of claims 1 to 12, which composition has been cured.

15. A process for fabricating a high voltage insulator, which comprises:

forming a mixture of a silicone rubber, a mineral filler, a curing agent for said silicone rubber and a silicone oil incompatible with said silicone rubber;

charging said mixture into a mould; and

applying heat to said mould thereby to cure said mixture into a solid elastomer having said liquid silicone oil dispersed throughout.

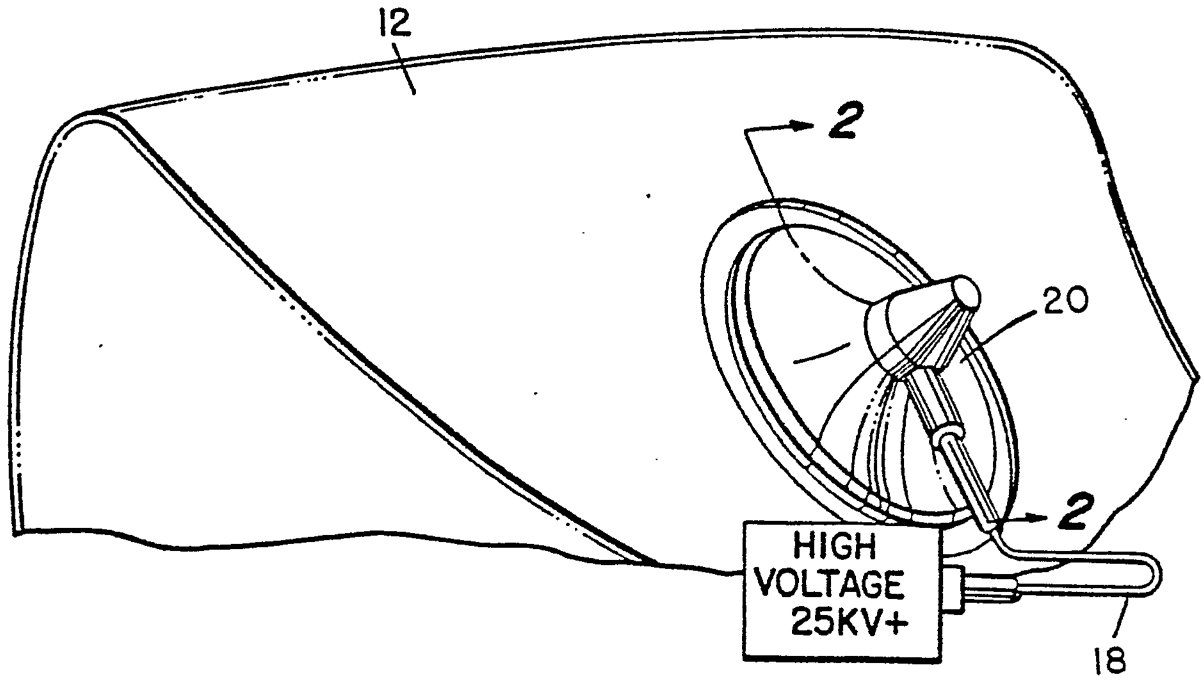

Fig. 1

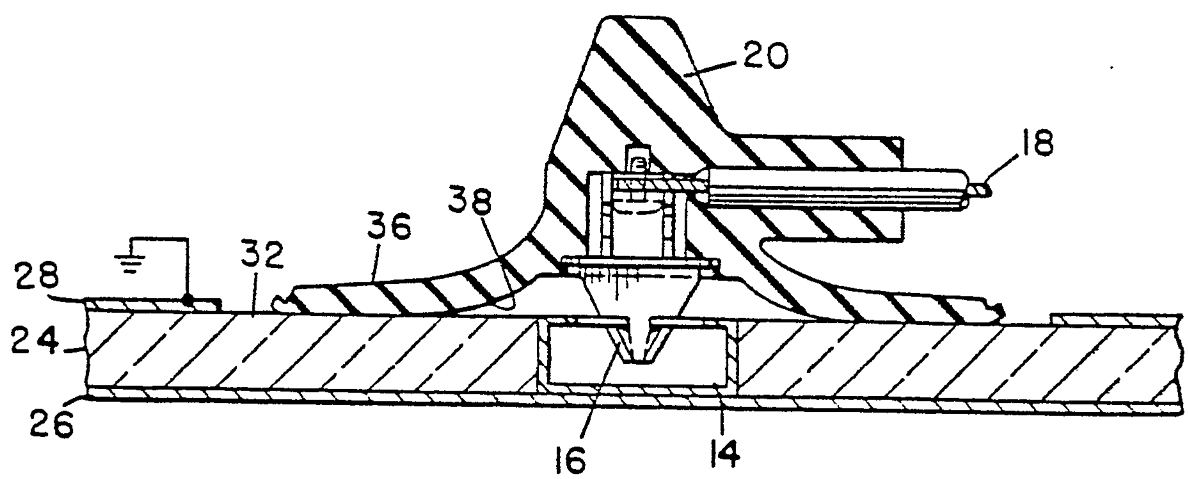

Fig. 2

0057098

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 82300358.7

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X,A	US - A - 3 795 646 (GENERAL ELECTRIC) * Abstract; claims 11,12 * --	1,2,4, 7,8,10-12,13
A	DE - B1 - 1 020 456 (DOW CORNING) * Claims; column 1, line 41 - column 4, line 36 * ----	1-13, 15

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

H 01 B 3/28
H 01 B 3/46
H 01 R 13/447
C 08 L 83/04
H 01 J 29/90
H 01 T 13/38

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

H 01 B 3/00
H 01 B 17/00
H 01 B 19/00
H 01 R 13/00
H 01 R 39/00
C 08 L 83/00
H 01 J 29/00
H 01 T 13/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	07-04-1982	KUTZELNIGG